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Determination of the Pre-bomb Southern (Antarctic) Ocean Radiocarbon in Organic Matter

T.P. Guilderson

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99-ERI-015 Final Report

The Southern Hemisphere is an important and unique region of the world's oceans for water-mass formation and mixing, upwelling, nutrient utilization, and carbon export. In fact, one of the primary interests of the oceanographic community is to decipher the climatic record of these processes in the source or sink terms for Southern Ocean surface waters in the CO_2 balance of the atmosphere. Current coupled ocean–atmosphere modeling efforts to trace the input of CO_2 into the ocean imply a strong sink of anthropogenic CO_2 in the southern ocean. However, because of its relative inaccessibility and the difficulty in directly measuring CO_2 fluxes in the Southern Ocean, these results are controversial at best.

An accepted diagnostic of the exchange of CO_2 between the atmosphere and ocean is the prebomb distribution of radiocarbon in the ocean and its time–history since atmospheric nuclear testing. Such histories of ^{14}C in the surface waters of the Southern Ocean do not currently exist, primarily because there are few continuous biological archives (e.g., in corals) such as those that have been used to monitor the ^{14}C history of the tropics and subtropics. One of the possible long-term archives is the scallop *Adamussium collbecki.* Although not independently confirmed, relatively crude growth rate estimates of *A. collbecki* indicate that it has the potential to provide continuous 100 year time-series. We are exploring the suitability of this potential archive.

One potential exploitable archive is the store of organisms collected over the last approximately 100 years as part of biological surveys and "routine" oceanographic surveys in the Southern Ocean. Most of these samples are preserved with formaldehyde, which acts to "harden" the organic matrix by cross-linking to proteins at an amine group. Since formaldehyde (usually as formalin) is a hydrocarbon product, the carbon isotopic chemistry is 14-C free or dead and has the potential to contaminate the original radiocarbon signature. To accurately recover the ^{14}C of the water, it is thus not possible to simply combust the specimens and convert the resulting CO_2 to graphite for standard radiocarbon analysis. Rather, to recover the "natural" ^{14}C signal embedded in these samples it is necessary to analyze only carbon atoms fixed by the organisms themselves.

The goal of this project was to develop a consistent methodology for recovering the natural ^{14}C signal in organic material collected from the Southern Ocean. Analysis of co-occurring JGOFS sediment trap sample splits that had been preserved with formalin, mercuric chloride, and sodium azide indicate that—at least for recently recovered bulk organic material—contamination in the formalin-preserved samples is not an issue: all of the values were similar within errors. To test the impact of long-term storage on radiocarbon signatures, we acquired (from the Auckland Museum in New Zealand) formalin-preserved samples (molluscs including shell and tissue) that had been collected in 1929 and 1930. We pretreated the organic material using "standard" protocol: after freeze drying a portion of the tissue it was finely ground and rinsed (3X) with deionized water, material was then vacuum dried in precombusted quartz tubes to which an aliquot of copper oxide was added, the tubes were evacuated and sealed,

combusted and the resulting CO_2 converted to graphite and analyzed. Carbonate material was treated by removing only the outermost edge (the most recently accreted material) of the shell with a microdrill. The resulting powder was then soaked in hydrogen peroxide, rinsed in deionized water and dried. Aliquots of the material were placed in individual vacutainers, evacuated to ~10^{-3} torr and acidified with the resulting CO_2 converted to graphite and analyzed. These analyses document a shift of nearly -100‰ in the bulk tissue samples relative to the carbonate, consistent with a ^{14}C-free formalin contaminant.

Radiocarbon analyses made on total lipid extracts from the same parent sample exhibit the same -100‰ shift observed in the bulk organic material. A comparison of bulk organic matter and lipid extract ^{14}C was made on recently collected (un-preserved) mussel tissue and the results are indistinguishable from each other. Thus, the lipids in the preserved samples are also contaminated either via direct binding, or in a more classic contamination sense whereby formalin is just present and we can't wash it all away. Attempts to recover free-proteins from the preserved samples not surprisingly proved negative.

We will utilize our newly upgraded sample-preparation laboratory to make additional compound-class organic extractions (amino acid, carbohydrate) from these same tissue samples to assess if individual compound classes are immune to the influence of ^{14}C contamination by formalin. A final test of whether or not we can ever recover the initial radiocarbon content of the organic matter will be to clip specific carboxyl chain carbons off individual amino acids, releasing the carboxyl carbon as CO_2 that can then be easily extracted and utilized for radiocarbon analyses. This procedure would have the benefit of physically separating the desired carbon from the organics and could (perhaps) circumvent any formalin contamination not just the formalin that has cross-linked with the proteins. If successful, we will obtain samples from the archives of organic specimens maintained by such museums as the Smithsonian Institution of Natural History and the American Museum of Natural History and begin mapping the prebomb distribution of radiocarbon in the surface waters of the Southern Ocean.

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